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TECHNICAL REPORT
71-39-FL

STORAGE STABILITY STUDIES ON RADIATION STERILIZED FISH ITEMS

by
R. O. Sinnhuber

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Oregon Agricultural Experiment Station,
Department of Food Science
and Technology,
Corvallis, Oregon 97331

Contract No. DA 19-129-AMC-853(N)

March 1971

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

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FOREWORD

Radiation processing, or "cold" sterilization as it is frequently called, has the potentiality of yielding seafood products that have good military utility, good storage stability, and good acceptability. Therefore, research to develop process criteria that can be used to produce irradiation sterilized seafoods is underway.

The work covered in this report was performed by Oregon State University under Contract No. DA 19-129-AMC-853(N) during the period from September 1965 to November 1967. It represents a series of studies on factors which are involved in non-enzymatic browning of irradiated codfish cakes, and the effects of selected anti-browning agents on the acceptability and storage stability of the product.

Professor R. O. Sinnhuber was the Project Officer and Official Investigator and Mrs. M. Landers the Collaborator in the research work for Oregon State University. The U.S. Army Natick Laboratories' Project Officer was Dr. F. Heiligman and the Alternate Project Officer was Dr. E. Wierbicki, both of the Food Laboratory. The work was conducted under Project 1C0-25601-A033, Radiation Preservation of Foods.

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ABSTRACT

Prevention of the "browning reaction" in radiation sterilized enzyme-inactivated and prefried cod patties during storage at 22°C for 12 months was investigated by several procedures which included leaching of the fish, the addition of browning inhibitors and low-temperature irradiation.

The browning reaction, as determined by visual and photometric means, may be partially controlled and lessened by leaching the fish and by the addition of certain browning inhibitors such as SO_2 and $CaCl_2$. However, these treatments did not necessarily improve flavor scores, as shown by panel evaluation.

Low-temperature irradiation did not materially affect color readings but did generally improve flavor scores.

The total-volatile-base values correlated with the treatment variables. The values increased with irradiation, storage at 22°C and the addition of browning inhibitors and decreased with leaching and low-temperature irradiation.

Our results indicated that it is possible to produce enzyme-inactivated and prefried patties which give acceptable flavor scores after storage for 12 months at 22°C.

STORAGE STABILITY STUDIES ON RADIATION STERILIZED FISH ITEMS

The objectives of this contract were to direct studies toward the causes, control and prevention of "browning" and other adverse changes that occur during storage of two irradiated codfish products, developed in our laboratory under previous U.S. Army Contracts DA 19-129-QM-1356 and DA 19-129-AMC-155(N). Various treatments included the use of selected browning inhibitors and antioxidants, leaching of the fish and irradiation at sub-zero temperature. The treatments were evaluated by chemical and physical techniques including color reflectance values, pH, 2-thiobarbituric acid number and total volatile bases. Subjective panel evaluations were obtained over a 12-month period of storage at 22°C. In addition, the effect of leaching and irradiation on ribose content of the fish was determined. An accelerated browning reaction test and 38°C storage tests were applied to a limited amount of patties to accelerate and predict probable color changes in the 22°C storage samples.

INTRODUCTION

A review of the literature concerning the "browning" reaction suggests that the non-enzymatic browning reaction in meat and fish is mainly due to the interaction of (1) reducing sugars and amines and (2) carbonyls and amines. Carbonyls originating from the autoxidation of fish lipids may play a lesser role in the browning reaction of cod, a low-fat fish.

It has been shown in previous work in our laboratory (1) that the production of carbonyls from irradiated fish lipids can be partially controlled by the addition of antioxidants to the sample. Reasonable success has been attained in the fruit and vegetable industry by the use of bisulfites to prevent the browning reaction by blocking the carbonyl group.

The reducing sugar and amine reaction may be controlled by the removal, or lessening the amount, of one of the reactants. The reducing sugars found in fish are mainly free ribose and ribose compounds, while glucose is found in lesser quantities. Free and bound ribose in fish muscle seem to be major components responsible for the browning reaction. Experiments were designed to minimize the browning reaction by removal or reduction of the soluble sugars by leaching the fish and the addition of bisulfite to block the reaction of the remaining sugars.

EXPERIMENTAL METHODS AND PROCEDURES

Frozen Pacific cod fillets (*Gadus macrocephalus*) were used in the preparation of all samples.

Leaching process, warm water method. Free ribose and most other ribose-containing compounds in fish (adenosine, ADP, ATP, inosine, etc.) are soluble in water, especially in warm water. A method was designed to

remove ribose from the fish by leaching with a large volume of water. Since the temperature of the water was kept at 77°C, the leaching process also inactivated enzymes present in the fish muscle (2). Five pounds of thawed cod were cut into small pieces and placed in a stainless steel basket lined with nylon press cloth. The basket was then placed in a double-jacketed steam kettle containing 6 liters of warm water at 77°C. Water temperature was maintained at 77°C for 10 minutes. Large pieces of fish were broken up by stirring with a wooden spoon. The basket was lifted out, the fish drained, and again rinsed with fresh warm water (38°C) and drained. Additives were incorporated in the leached fish while still warm. This leaching method was used in preliminary storage studies at 22° and 38°C and the accelerated browning reaction test.

Leaching process, cold water method. A simpler leaching method, and as effective as the warm water method, was devised for preparation of the 12-month storage samples and utilized a cold saline solution. Thirty pounds of cod were ground in a meat grinder with a 1/4 inch plate and added to 50 pounds of cold water containing 0.9% salt, with constant stirring. The fish was drained in a nylon bag. The leaching process was repeated two more times, so that the total leaching water was five times the weight of the fish. The leached fish was allowed to drain overnight in a cool room (1°C) and the final moisture content varied

from 81.5 to 85.5%. Moisture content was adjusted to 85.5% prior to preparation of the fish patties to assure a uniform product.

Preliminary storage studies at 22° and 38°C. Fish patties were prepared from leached and unleached fish. To some samples SO_2 in the form of sodium metabisulfite, 0.4% $CaCl_2$, ribose, binders or 50 ppm antioxidants (Tenox-6, Eastman Chemical Products, Inc., Kingsport, Tennessee, containing 10% butylated hydroxyanisole, 10% butylated hydroxytoluene, 6% propyl gallate, 6% citric acid, 12% propylene glycol and 56% vegetable oil) were added. The leached fish patties were prepared by the warm water method and the following binder formulation was added to some of the samples: 5.0% white corn meal, 1.5% Viscomix gelatin (Swift and Co.), 1.0% salt, 0.15% monosodium glutamate (MSG) and 10.0% water. The binder mixture was heated in a boiling water bath to a temperature of 82°C, added to the warm leached fish and mixed thoroughly. The fish was passed through an electric grinder without the cutter blade, stuffed in sausage casings having a diameter of 2-1/2 inches, frozen at -28°C and sliced in 3/8 inch thick patties. The patties were packed in "C" enamelled cans, sealed under 26 inch vacuum and stored frozen until irradiation. Eleven treatments were evaluated by visual color observations by three judges after irradiation and storage of the samples at 22° and 38°C.

Accelerated browning reaction test. The rate of the browning reaction is dependent on the storage temperature of the sample. Fish stored at

freezing temperature may remain unchanged in color for a long period of time, but develop a yellow to brown discoloration, depending on sugar content, in one hour if heated to 120°C. This accelerated testing method, as described by Tarr (3), was employed for immediate evaluation of the effectiveness of various treatments such as irradiation temperature, leaching and the addition of antioxidants and sulfites. The treated ground fish sample (approximately 10 grams) was placed in a test tube, covered with aluminum foil and heated in an autoclave at 15 pounds steam pressure for 1 hour.

Determination of reducing sugars. The fish tissue was extracted with perchloric acid (4) and bound ribose was removed from the extract as described by Miyauchi *et al*. (5). Free ribose in the extract was analyzed by the method of Mejbaum (6). Total ribose was determined by the trichloroacetic acid extraction method described by Hamoir (7). The same extract was also used to determine the glucose content by the anthrone method of Bartlett (8).

Effect of sulfites on antioxidants. Previously (1), Tenox-6 was found to be an effective antioxidant mixture that protected lipids in irradiated fish from autoxidation. However, the efficiency of the antioxidants may be affected by the presence of such reactive compounds as sulfites and bisulfites. An accelerated fat oxidation test, the Active Oxygen Method (AOM) (9), was used to test the effect of added

bisulfite on Tenox-6, using lard as a substrate. Sulfur dioxide (400 ppm) was added to lard containing 0.02% antioxidants.

Preparation of products for 12-months storage at 22°C.

1. Enzyme-inactivated cod patties. To each 100 pounds of ground fish, leached or unleached, was added 4 pounds white corn meal, 1.5 pounds Viscomix gelatin, 0.4 pound salt, 0.2 pound MSG and 50 ppm antioxidants (Tenox-6). Sulfur dioxide (500 ppm) and 0.4% calcium chloride were added as browning inhibitors to some of the test samples. The ground fish was stuffed in meat casings, cooked in a boiling water bath to enzyme-inactivation temperature of 71°C for 15 seconds, cooled, quick-frozen at -28°C, sliced into patties and packed in 307 x 409 "C" enamelled cans for irradiation. Parchment paper separated the patties and protected the four 1-gram charcoal packets attached to the underside of the lid. The cans were sealed under 26 inch vacuum and stored frozen until irradiation, approximately one month.

2. Prefried cod patties. Preparation of the prefried cod patties was as described for the enzyme-inactivated patties with the following changes: Salt (0.4%) and 50 ppm antioxidants (Tenox-6) were added to the leached and unleached ground cod; after slicing, the patties were dipped in batter mix, breaded and deep-fried in hydrogenated shortening at 182°C for approximately three minutes (minimum internal temperature, 71°C).

The nine treatments or variables that were evaluated were the same for both the enzyme-inactivated and the prefried cod patties and included leaching of the fish, the use of browning inhibitors and low temperature irradiation. The treatments are presented in Table 1.

Table 1. Treatment Variables in the Evaluation of Radiation Sterilized Cod Patties

Sample	Leaching	Browning inhibitors	Irradiation level (Mrad)	Irradiation temperature
1	-	-	0	-
2	-	-	4.5	ambient
3	-	-	4.5	-40°C
4	-	+	4.5	ambient
5*	-	+	4.5	-40°C
6	+	-	4.5	ambient
7*	+	-	4.5	-40°C
8	+	+	4.5	ambient
9*	+	+	4.5	-40°C

* Limited amount of sample for small panel evaluation.

Irradiation procedure. The frozen samples were shipped under dry ice, via Air Freight, to the Co-60 source at Natick, Massachusetts, for irradiation at 4.5 Mrad. The dose rate was 3.65×10^4 rads/min and the dwell time was approximately 123 minutes, with a minimum dose received of 4.5 Mrad to a maximum of 5.6 Mrad. One lot of fish was irradiated at -40°C (±10°C) and held frozen for the return shipment to Oregon State University. The remaining samples were irradiated at ambient temperature and were approximately 1°C at the beginning of irradiation and reached a maximum temperature of 50°C at the end of the run. These samples were returned under ambient conditions. The time interval between irradiation and start of 22°C storage was two weeks.

Storage conditions. The fish patties were stored in controlled temperature rooms operating at 20°-22°C for 0, 4, 8 and 12 months. The non-irradiated control samples were held at -22°C.

Flavor panel evaluations. Large student panels (100) and small staff panels (20-24) evaluated the enzyme-inactivated and prefried cod patties. The large panel evaluated 6 storage treatments of each product, including 1 patty irradiated at low temperature.

Mouse lethality tests for the detection of Clostridium botulinum toxin were conducted on all samples prior to presentation for panel evaluation to assure their safety. A composite sample for each treatment was prepared by taking samples from each can. No samples were lethal to mice.

The enzyme-inactivated patties were breaded and deep-fried at 182°C (365°F) for 3 minutes at time of serving. The prefried patties were heated in a 204°C (400°F) oven for 15 minutes to serve. The tasters were seated in individual booths, illuminated by white light, and were served the samples in randomly coded paper cups (1/4 patty per treatment). The 9-point hedonic ballot was used and all flavor data were analyzed by analysis of variance at the 5% significance level.

Objective methods of evaluation. Total volatile bases (10), 2-thiobarbituric acid number (11), sulfur dioxide content (12), pH and color reflectance values of the cod patties were determined at each storage period. The pH was measured with a Beckman Zeromatic pH meter using 10 grams of samples mixed with 10 milliliters distilled water. Color reflectance readings were obtained with a photoelectric reflection meter, Model 610 (Photovolt Corp., New York, N. Y.) using a tri-green filter. Color reflectance readings are presented as percent reflectance values and are the average of three readings from three cakes per treatment. The prefried patties were sliced horizontally for a reading of the fish flesh.

RESULTS AND DISCUSSION

Determination of reducing sugars. The leaching process removed considerable quantities of reducing sugars from the fish as shown in

Table 2. Irradiation at 4.5 Mrad caused no significant change in ribose content of the leached fish.

Table 2. Reducing Sugars in Cod Fish Samples

Treatment	Total ribose µg/g fish	Free ribose µg/g fish	Glucose µg/g fish
Unleached	1495	104	401
Leached	275	19	117
Leached, irradiated	258	19	-

Accelerated browning reaction test. Results of the accelerated browning reaction test for irradiated and non-irradiated samples are given in Table 3. The unleached samples developed brown color during the heating test and the addition of bisulfite and antioxidants, singly or in combination, were not sufficent to retard the browning reaction for either the irradiated or non-irradiated samples. The leached samples were white or light yellow after heating. However, the addition of ribose to the leached fish caused browning when heated. The leached, irradiated samples showed varied color changes after the heat test, from white to light brown. The leached sample containing antioxidants,

binders, 500 ppm SO_2 and 0.4% $CaCl_2$ remained white after heating for 6 hours at 120°C and after irradiation and heating.

Preliminary storage studies at 22° and 38°C. Visual color evaluations of irradiated fish patties stored at 22° or 38°C for up to 300 days are recorded in Table 4. There were two distinct color changes in the stored samples. The unleached samples developed the customary yellow to tan coloration usually associated with the browning reaction; the leached sample containing no additives exhibited a light yellow color change, while the leached samples with additives tended to go from white to grey. The greyish-white color may be due in part to reaction of propyl gallate present in the antioxidant mixture. An exception to this color change was the leached sample containing antioxidants and binders, but no SO_2, which became brown after storage for 300 days at 38°C.

Effect of sulfites on antioxidants. The effect of sulfite added to lard containing antioxidants on the AOM stability is shown in Table 5. The number of hours required to reach a peroxide value of 100 meq/kg sample was used as the end point.

Table 3. Color Changes of Cod Fish Samples During the Accelerated Browning Reaction Test

Treatment	Non-irradiated	Irradiated
Unleached control	Brown	Brown
+ 250 ppm SO_2	Brown	Brown
+ A[a]	Brown	Brown
+ 250 ppm SO_2 + A	Brown	Brown
Leached control	Off-white	Light brown
+ ribose (200 µg/g)	Brown	-
+ A	Off-white	Light brown
+ A + B[b] + 250 ppm SO_2	White	Light tan
+ A + B + 250 ppm SO_2 + ribose	White	-
+ A + B + 250 ppm SO_2 + 0.4% $CaCl_2$	White (2 hr)[c]	Yellow
+ A + B + 500 ppm SO_2 + 0.4% $CaCl_2$	White (6 hr)[c]	White

[a] Antioxidant mixture.

[b] Binder mixture.

[c] Color remained white after 2 hours or 6 hours heating at 120°C.

Table 4. Color Changes[a] of Radiation Sterilized Fish Patties at Two Storage Temperatures

Treatment	Storage time (days) 22°C: 106	22°C: 300	38°C: 106	38°C: 150	38°C: 208	38°C: 300
Unleached cod						
Control	ly	y	lt	lt	t	t
+ A[b] + 250 ppm SO_2	ly	ly	y	y	lt	t
+ A + 1000 ppm SO_2	ly	ly	y	y	lt	y
Leached cod						
Control	ly	ly	ly	ly	ly	ly
+ A	lg	lg	w	lg	lg	lg
+ A + 250 ppm SO_2	w	w	w	lg	lg	lg
+ A + 500 ppm SO_2	w	lg	lg	lg	lg	lg
+ A + 1000 ppm SO_2	w	g	w	lg	lg	-
+ A + B[c]	ly	y	y	t	b	b
+ A + B + 250 ppm SO_2	lg	g	w	lg	g	g
+ A + B + 500 ppm SO_2 + 0.4% $CaCl_2$	w	lg	lg	g	g	-

[a] Colors: l - light; y - yellow; w - white; g - grey; t - tan; b - brown.

[b] Antioxidant mixture.

[c] Binder mixture.

Table 5. The Effect of Sulfite and Antioxidants on the Stability of Lard

Treatment	AOM hours
Lard, control	6.60
Lard + 400 ppm SO_2	3.80
Lard + 0.02% antioxidants	98.30
Lard + 0.02% antioxidants + 400 ppm SO_2	81.90

The addition of SO_2 to lard decreased the AOM stability of the lard by about 42.4%, probably by destruction of the natural antioxidants. However, the addition of SO_2 to lard containing Tenox-6 reduced the AOM stability by only 16% as compared to the lard sample containing Tenox-6 alone. Antioxidants appeared to be effective in counteracting the adverse effects of SO_2 on the stability of the lard.

Storage studies for twelve months at 22°C.

1. Flavor panel evaluations. Mean flavor scores for enzyme-inactivated cod patties are given in Table 6. Initially large panel evaluation showed no significant difference in flavor scores between the non-irradiated control and the unleached sample without browning inhibitors and irradiated at -40°C. All other treatments were judged significantly

Table 6. Mean Flavor Scores[a] for Radiation Sterilized Enzyme-inactivated Cod Patties Stored at 22°C

Treatment	Radiation temp. °C	Storage time (months): 0, Large panel	0, Small panel	4, Small panel	8, Small panel	12, Small panel
Control (0 Mrad, -22°C)						
Unleached	-	6.5	7.1	6.6	6.8	6.8
4.5 Mrad						
Unleached	ambient	6.0*	6.6	6.0	6.1	5.1*
Unleached	-40°C	6.4	6.3	6.8	6.7	5.9
Unleached + BI[b]	ambient	5.6*	5.9*	5.5*	6.0	4.8*
Unleached + BI	-40°C	-	5.1*	5.3*	5.1*	4.9*
Leached	ambient	5.2*	5.2*	5.8	5.4*	4.8*
Leached	-40°C	-	5.4*	6.0	5.8*	5.2*
Leached + BI	ambient	5.3*	4.5*	5.8	5.9	5.7*
Leached + BI	-40°C	-	6.1	6.1	5.6*	5.0*

[a] Score 9 high, 1 low.

[b] Browning inhibitors - 500 ppm SO_2 + 0.4% $CaCl_2$.

* Significantly different from the control at 5% significance level.

lower than the control. A small panel gave similar results after 12 months storage at 22°C. As has been noted before, there seemed to be an improvement in flavor scores after a short period of storage (4 months) at room temperature. This is believed to be due to the loss of irradiated odor and flavor. Five of the irradiated samples received "acceptable" flavor scores (5.0 or above) after 12 months storage at 22°C.

Leaching of the fish in enzyme-inactivated patties significantly improved flavor scores of the irradiated patties after 12 months storage when the sample contained browning inhibitors and was irradiated at ambient temperature. Low-temperature irradiation had no effect on flavor scores between comparable treatments. The addition of browning inhibitors lowered the flavor scores of the unleached sample irradiated at -40°C and significantly improved the flavor score of leached sample at ambient radiation.

Mean flavor scores for prefried cod patties are shown in Table 7. At the beginning of storage all irradiated samples received significantly lower scores than the control, with the exception of the small panel mean flavor score for the unleached patty containing no browning inhibitors and irradiated at ambient temperature. After 12 months storage the small panel scored the leached patty containing no browning

Table 7. Mean Flavor Scores[a] for Radiation Sterilized Prefried Cod Patties Storage at 22°C

Treatment	Radiation temp. °C	Storage time (months)				
		0	0	4	8	12
		Large panel	Small panel			
Control (0 Mrad, -22°C)						
Unleached	-	6.6	6.7	7.0	5.9	6.3
4.5 Mrad						
Unleached	ambient	5.7*	5.8	5.6*	4.8*	4.5*
Unleached	-40°C	5.9*	5.6*	6.0*	5.7	5.3*
Unleached + BI[b]	ambient	4.8*	4.8*	4.4*	4.8*	5.1*
Unleached + BI	-40°C	-	5.5*	4.8*	4.5*	4.5*
Leached	ambient	5.4*	5.0*	5.0*	4.5*	4.4*
Leached	-40°C	-	5.0*	5.3*	5.5	5.8
Leached + BI	ambient	5.2*	5.1*	5.3*	5.2	5.0*
Leached + BI	-40°C	-	4.6*	4.7*	5.0	5.3*

[a] Score 9 high, 1 low.

[b] Browning inhibitors - 500 ppm SO_2 + 0.4% $CaCl_2$.

* Significantly different from control at 5% significance level.

inhibitors and irradiated at $-40^{\circ}C$ was not significantly different from the non-irradiated control. Five of the irradiated samples scored on the "like" side of the hedonic scale.

Leaching of the fish in prefried patties gave no significant differences in flavor scores of the irradiated samples after 12 months storage between samples irradiated at ambient and $-40^{\circ}C$, or with and without the addition of antioxidants. Low-temperature irradiation significantly improved the mean flavor score for the leached sample without browning inhibitors. The addition of browning inhibitors had no effect on flavor scores between samples treated in a similar manner.

2. Objective methods of evaluation. Total volatile bases (TVB) are given in Table 8, TBA numbers for enzyme-inactivated cod patties in Table 9, pH values in Table 10, sulfur dioxide values in Table 11 and color reflectance readings in Table 12.

Table 8. Total Volatile Base Determinations[a] of Radiation Sterilized Cod Patties During 22°C Storage

Treatment	Radiation temp. °C	Storage time (months)							
		0	4	8	12	0	4	8	12
		Enzyme-inactivated patties				Prefried patties			
0 Mrad, -22°C									
Unleached	-	6.49	10.68	10.90	11.03	11.20	10.33	10.33	10.50
4.5 Mrad									
Unleached	ambient	13.21	25.90	30.10	30.80	21.70	28.00	32.90	36.05
Unleached	-40°C	7.18	18.20	20.13	24.50	13.65	21.70	25.38	33.95
Unleached + BI[b]	ambient	30.37	39.03	42.70	46.38	32.75	41.30	44.80	47.43
Unleached + BI	-40°C	23.72	32.90	35.53	38.85	23.80	33.60	42.70	46.90
Leached	ambient	4.80	15.93	17.85	19.60	5.95	9.98	10.50	11.90
Leached	-40°C	4.59	8.05	11.20	13.13	2.80	5.75	8.75	9.63
Leached + BI	ambient	11.11	15.40	17.50	18.81	5.95	11.03	12.60	14.18
Leached + BI	-40°C	7.35	12.25	14.35	15.31	6.65	9.28	11.90	13.48

[a] mgN/100 g fish.

[b] Browning inhibitors - 500 ppm SO_2 + 0.4% $CaCl_2$.

Table 9. TBA Numbers[a] of Enzyme-inactivated Cod Patties During 22°C Storage

Treatment	Radiation temp. °C	Storage time (months) 0	4	8	12
0 Mrad, -22°C					
Unleached	-	0.70	0.51	0.94	0.97
4.5 Mrad					
Unleached	ambient	1.08	0.62	0.86	0.81
Unleached	-40°C	0.65	0.67	0.70	0.69
Unleached + BI[b]	ambient	0.65	0.61	0.85	0.49
Unleached + BI	-40°C	0.65	0.73	0.71	0.63
Leached	ambient	0.49	0.58	0.79	0.71
Leached	-40°C	0.58	0.66	0.77	0.64
Leached + BI	ambient	0.73	0.52	0.74	0.71
Leached + BI	-40°C	0.69	0.66	0.86	0.53

[a] mg malonaldehyde/1000 g fish.

[b] Browning inhibitors.

Table 10. pH Values of Radiation Sterilized Enzyme-inactivated Cod Patties During 22°C Storage

Treatment	Radiation temp. °C	Storage time (months)							
		Enzyme-inactivated patties				Prefried patties			
		0	4	8	12	0	4	8	12
0 Mrad, -22°C									
Unleached	-	6.8	6.8	6.8	6.8	6.6	6.6	6.6	6.5
4.5 Mrad									
Unleached	ambient	6.9	6.9	6.9	6.9	6.6	6.6	6.7	6.7
Unleached	-40°C	6.9	6.9	6.9	6.9	6.7	6.7	6.7	6.7
Unleached + BI[a]	ambient	6.8	6.8	6.8	6.8	6.5	6.4	6.6	6.5
Unleached + BI	-40°C	6.7	6.8	6.7	6.8	6.6	6.6	6.5	6.5
Leached	ambient	6.8	6.8	6.8	6.8	6.2	6.1	6.2	6.1
Leached	-40°C	6.9	6.9	6.9	6.9	6.3	6.1	6.1	6.2
Leached + BI	ambient	6.5	6.5	6.6	6.5	6.5	6.5	6.4	6.4
Leached + BI	-40°C	6.5	6.5	6.5	6.5	6.4	6.5	6.5	6.5

[a] Browning inhibitors.

Table 11. Residual Sulfur Dioxide Content[a] in Radiation Sterilized Cod Patties During 22°C Storage

Treatment	Radiation temp. °C	After radiation Storage time (months) 0	4	8	12
Enzyme-inactivated					
Unleached	ambient	107	87	99	87
Unleached	-40°C	88	100	128	135
Leached	ambient	45	32	23	20
Leached	-40°C	135	81	80	77
Prefried					
Unleached	ambient	78	39	30	29
Unleached	-40°C	100	62	30	30
Leached	ambient	85	94	81	103
Leached	-40°C	203	140	141	127

[a] SO_2 reported in ppm, 500 ppm added to each sample.

Table 12. Color Reflectance Values[a] of Radiation Sterilized Cod Patties During 22°C Storage

Treatment	Radiation temp. °C	Storage time (months)							
		0	4	8	12	0	4	8	12
		Enzyme-inactivated patties				Prefried patties			
0 Mrad, -22°C									
Unleached	-	55	52	53	51	51	49	55	54
4.5 Mrad									
Unleached	ambient	46	44	42	43	52	43	38	39
Unleached	-40°C	50	47	47	49	56	46	40	38
Unleached + BI[b]	ambient	46	42	52	49	59	55	48	44
Unleached + BI	-40°C	50	43	51	49	58	53	44	43
Leached	ambient	46	41	38	41	54	54	45	45
Leached	-40°C	43	45	44	41	61	55	46	47
Leached + BI	ambient	58	55	51	55	63	59	53	51
Leached + BI	-40°C	48	55	50	53	60	56	52	53

[a] Percent reflectance, higher values indicate lighter color.

[b] Browning inhibitors - 500 ppm SO_2 + 0.4% $CaCl_2$.

Total volatile bases increased with storage for each treatment. The leached samples had lower TVB values than the unleached samples. In the enzyme-inactivated samples after 12 months storage the leached samples irradiated at -40°C had values comparable to the control. All leached prefried patties had values comparable to the control after storage. The highest values were obtained in the unleached samples containing browning inhibitors. All values were lowered in similarly treated samples when temperature of irradiation was lowered.

TBA number and pH values changed only slightly during storage of the samples and seemed to have little value as indicators of quality of irradiated stored cod products.

Sulfur dioxide content was generally lower in samples irradiated at ambient temperature than in similarly treated samples irradiated at -40°C. Leached samples had higher SO_2 values than the unleached samples in the prefried patties while the reverse was true for enzyme-inactivated patties.

Color reflectance values indicated a greater degree of browning in the prefried patties than in the enzyme-inactivated patties during 12 months storage at 22°C. Both enzyme-inactivated and prefried patties which had been leached and contained browning inhibitors were similar in color to the controls after storage. Other treatments showed varying degrees of

browning. The addition of browning inhibitors and leaching of the fish generally retarded browning while low-temperature irradiation had little effect.

REFERENCES

1. SERRANO, L. B. 1964. Determination of the quality of radiation-pasteurized halibut (Hippoglossus stenolepsis) during storage. M. S. thesis, Oregon State University, Corvallis, Oregon.

2. SINNHUBER, R. O. and LANDERS, M. K. 1964. Enzyme-inactivation studies on irradiation-sterilized cod fillets. J. Food Sci. 29, 190-191.

3. TARR, H. L. A. 1950. The Maillard reaction in fish products. J. Fish. Res. Bd. Canada 8, 74-81.

4. SPINELLI, J., EKLUND, M. and MIYAUCHI, D. 1964. Measurements of hypoxanthine in fish as a method of assessing freshness. J. Food Sci. 29, 710-714.

5. MIYAUCHI, D., SPINELLI, J., PELROY, G. and STOLL, N. November, 1965. Application of radiation pasteurization processes to Pacific crab and flounder. Report No. TID-4500. pp. 61. Technical Service Dept. of Commerce, Washington, D. C. 20230.

6. MEJBAUM, W. 1939. Uber die bestimmung kleiner pentosemengen, insbesondere in derivaten der adenylsauer. Z. Physiol. Chem. 258, 117-120.

7. HAMOIR, G. 1951. Fish tropomyosin and fish nucleotropomyosin. Biochem. J. 48, 146-151.

8. BARTLETT, G. R. 1959. Methods for the isolation of glycolytic intermediates by column chromatography with ion exchange resins. J. Biol. Chem. 234, 459-465.

9. AOCS OFFICIAL AND TENTATIVE METHODS. 1966. Fat Stability, Active Oxygen Method Cd 12-57.

10. STANSBY, M. E., HARRISON, R. W., DASSOW, J., and SATER, M. 1944. Determining volatile bases in fish. Ind. Eng. Chem. Anal. Ed. 16, 593.

11. SINNHUBER, R. O. and YU, T. C. 1958. Characterization of the red pigment formed in the 2-thiobarbituric acid determination of oxidative rancidity. Fd. Res. 23, 626.

12. AOAC. 1960. Official Methods of Analysis, procedure 27.081. 10th ed. Assoc. of Official Agr. Chemists, Washington, D. C.

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13. ABSTRACT

Prevention of the "browning reaction" in radiation sterilized enzyme-inactivated and prefried cod patties during storage at 22°C for 12 months was investigated by several procedures which included leaching of the fish, the addition of browning inhibitors and low-temperature irradiation.

The browning reaction, as determined by visual and photometric means, may be partially controlled and lessened by leaching the fish and by the addition of certain browning inhibitors such as SO_2 and $CaCl_2$. However, these treatments did not necessarily improve flavor scores, as shown by panel evaluation.

Low-temperature irradiation did not materially affect color readings but did generally improve flavor scores.

The total-volatile-base values correlated with the treatment variables. The values increased with irradiation, storage at 22°C and the addition of browning inhibitors and decreased with leaching and low-temperature irradiation.

Our results indicated that it is possible to produce enzyme-inactivated and prefried patties which give acceptable flavor scores after storage for 12 months at 22°C.

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Cod	9		9			
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Enzyme inhibitors			6			
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